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Study of paramagnetic defect centers in as-grown and annealed TiO_2 anatase and rutile nanoparticles by a variable-temperature X-band and high-frequency (236 GHz) EPR

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ABSTRACT

Detailed EPR investigations on as-grown and annealed TiO_2 nanoparticles in the anatase and rutile phases were carried out at X-band (9.6 GHz) at 77, 120–300 K and at 236 GHz at 292 K. The analysis of EPR data for as-grown and annealed anatase and rutile samples revealed the presence of several paramagnetic centers: Ti^{3+}, O^-, adsorbed oxygen ($O_2{}^-$) and oxygen vacancies. On the other hand, in as-grown rutile samples, there were observed EPR lines due to adsorbed oxygen ($O_2{}^-$) and the Fe^{3+} ions in both Ti^{4+} substitutional positions, with and without coupling to an oxygen vacancy in the near neighborhood. Anatase nanoparticles were completely converted to rutile phase when annealed at 1000° C, exhibiting EPR spectra similar to those exhibited by the as-grown rutile nanoparticles. The high-frequency (236 GHz) EPR data on anatase and rutile samples, recorded in the region about $g=2.0$ exhibit resolved EPR lines, due to O^- and $O_2{}^-$ ions enabling determination of their g-values with higher precision, as well as observation of hyperfine sextets due to Mn^{2+} and Mn^{4+} ions in anatase.

1. Introduction

Nanosize titanium dioxide (TiO_2) exists at room temperature in different phases, namely anatase, rutile and brookite. Pure single crystals of TiO_2 exist only in rutile structural phase. On the other hand, only Fe^{3+}, Al^{3+}, Mg^{2+} impurities can stabilize anatase and Mg^{2+} impurity stabilizes brookite phase [1,2]. TiO_2 nanoparticles have received considera Prod. Type: FTPble attention from material researchers due to its interesting properties and many technical applications. For example, TiO_2 nanoparticles find usage in paint (as pigments) [3], cosmetics [4], dielectrics [5], electrochromics [6], organic depollutant on windows [7], water/air purifier and deodorizer [8], lithium-ion batteries [9], dye-sensitized solar cells [10], gas sensors [11], catalyst supports [12], photocatalysis [13], photo voltaic cells [14], luminescent [15], biomaterials [16]. Such a vast range of applications is possible due to the two commonly occurring polymorphs of TiO_2, rutile and anatase, which are significantly different in their physical and electronic properties [17]. Particle size, besides other parameters, plays an important role in determining the properties of TiO_2. For example, energy bandgap of bulk anatase is about 3.2 eV, while the 5–10 nm size anatase particle exhibits a band gap which is~0.1–0.2 eV higher than that of bulk anatase [17]. This bandgap increase gives an advantage to nanosized TiO_2 over the bulk TiO_2 in some specific applications where increased band gap is required, an example being photovoltaic devices. Recently ferromagnetism up to 880 K was found both in thin films of TiO_2 [18] and nanoparticles of TiO_2 [17]. It was found, that saturation magnetization increased with long annealing in vacuum. The ferromagnetism disappears after annealing in oxygen atmosphere, being converted to the paramagnetic state [19]. Several methods of synthesis of TiO_2 nanoparticles have been reported in the literature, e.g., sol–gel [20], hydrothermal [21], citrate-gel [22], hydrolysis [23], or gas-phase pyrolysis of titanium tetrachloride [24], direct oxidation of titanium platelets [25], metal organic chemical vapor deposition (MOCVD) [26].

It is interesting to compare the properties of anatase and rutile nanoparticles, which possess such different surface morphologies. The technique of electron paramagnetic resonance (EPR) is very sensitive to the investigation of defects or paramagnetic centers in oxides, and thus quite capable of revealing such differences. The present paper is devoted to a detailed EPR study of as-grown anatase and rutile samples, as well those of annealed samples. The

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